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(54) Title: COATING COMPOSITIONS CONTAINING URETHANE AND EPOXY COMPONENTS AND ARTICLES COATED THEREOF (57) Abstract An article is provided consisting of an epoxy base coat and a urethane top coat which is useful in pavement marking applications. The epoxy composition is a two-part, 100 percent volatile free system containing one or more hardeners which are reacted with an epoxy component such as the glycidyl ether of bisphenol-A. The urethane composition is also a two-part, 100 percent volatile free system containing a polyisocyanate component and an intermediate component comprising a polylactone polyol, and/or a polyether polyol, a polyester polyol, or a polyether-ester polyol, an aliphatic polyol chain extender and a moisture scavenger. The two-part epoxy composition can be applied to a road with the urethane composition coated thereof whereupon it serves as a lane marker. The urethane composition exhibits weatherability and abrasion-resistance and has non-yellowing characteristics. Various reflective compounds such as glass beads can be applied and partially embedded therein to provide night and wet night reflectivity.		

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"COATING COMPOSITIONS CONTAINING URETHANE AND
EPOXY COMPONENTS AND ARTICLES COATED THEREOF"

FIELD OF THE INVENTION

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The present invention relates to generally a volatile-free, two-part, epoxy composition, and to generally a volatile-free, two-part, urethane composition, and to an article made therefrom by generally coating the urethane composition on the epoxy composition.

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BACKGROUND OF THE INVENTION

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U.S. Patent No. 3,136,733 to Ross et al relates to highway marking material adapted for marking pavements of roads, streets, highways, aircraft landing strips, and the like, for defining traffic lanes, pedestrian cross-walks, traffic instructions, and the like.

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U.S. Patent No. 4,554,214 to Ichinomiya et al relates to a polyurethane type casting coating which is used as labelling materials in labels, stickers, outdoor signs, reflective refractors, light road markings or automobiles.

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U.S. Patent No. 4,689,268 to Meader, Jr. relates to a concrete surface coated with a cast in place surfacing composition comprising at least three layers, in order from the concrete surface:

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a first layer comprising:

1) a hard, epoxy resin, and

2) an inert, organic filler material consisting essentially of hollow ceramic beads;

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a second layer comprising a bonding agent which improves adhesion between said first and third layers, and;

a third layer comprising: (1) 20 to 80 parts by weight of a polyurethane, said polyurethane formed by

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5 reacting a polyisocyanate with a polyurethane precursor at a mole ratio of 0.8 to 1.4:1, said polyurethane precursor comprising 15 to 60 parts by weight of a high molecular weight polyol and 2 to 10 parts by weight of a low molecular weight chain stiffener, (2) 20 to 80 parts by weight of a substantially non-volatile extender, and (3) 0 to 20 parts by weight of a volatile solvent.

10 U.S. Patent No. 4,699,814 to Ambrose et al relates to an improved process of preparing color-plus-clear coatings, the improvement comprising an epoxy-functional polyurethane resin and high solids thermosetting coating compositions prepared therewith.

15 U.S. Patent No. 4,732,790 to Blackburn et al relates to an improved process for preparing color-plus-clear coatings, the improvement comprising high solids thermosetting coating compositions comprising hydroxy-functional polyepoxides and anhydrides as effective curing agents therefor. Films of these coating compositions have low volatile organic content (VOC).

20 U.S. Patent No. 4,758,469 to Lange relates to pavement marking comprising ceramic microspheres held by a binder, said microspheres being solid, transparent, non-vitreous, ceramic particles which serve as lens elements in the retro reflective pavement markings. The ceramic microspheres formed by various sol gel techniques are characterized by having at least one metal oxide phase; and an average minimum dimension of up to 125 micrometers.

30 U.S. Patent No. 4,837,069 to Bescup et al relates to a procedure for making Al_2O_3 spheroids, 600 micrometers in diameter or less, utilizing an AlOOH sol containing 0.25 percent weight percent MgO (in the form of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and HNO_3 . The sol is dispersed into droplets in a particle forming fluid (e.g., 2-ethylhexanol) where gelling occurs. The gelled spheroids are collected, dried and pre-fired in air at

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temperatures less than 1,200°C for up to about 12 hours. The dried and prefired beads are fired in a 2-step process at temperatures of about 1,850-1,950°C in the following sequence: a first dry oxygen firing for about ten minutes, followed by a wet hydrogen firing for up to 350 minutes. Reasonably transparent microspheres having crystallites in the range of 5-100 micrometers are obtained with little intergranular porosity, and their density is estimated to be near theoretical.

U.S. Patent No. 4,855,185 to Vu et al relates to novel polyurethane formulations especially useful as membranes for the protection of bridge deckings. The polyurethane is prepared by mixing two components, A and B. Component A consists essentially of a low molecular weight polyol, e.g., glycerol; a poly(oxypropylene) triol; and an elastomer. Component B is a special MDI, either a mix of 4,4'- and 2,4'-isomers of diphenylmethane diisocyanate or a mix of 4,4'-diphenylmethane diisocyanate and its reaction product with a low molecular weight poly(oxypropylene).

U.S. Patent No. 4,859,735 to Vu relates to novel polyurethane formulations especially useful as membranes of the protection of bridge deckings. The polyurethane is prepared by mixing two components, A and B. Component A comprises castor oil modified with a ketone-formaldehyde condensate and also preferably contains an elastomer. Component B is a modified MDI, being a mixture of diphenylmethane diisocyanate and its reaction product with a low molecular weight poly(oxyalkylene).

U.S. Patent No. 4,877,829 to Vu et al relates to novel polyurethane formulations especially useful as membranes for the protection of bridge deckings. The polyurethane is prepared by mixing two components, A and B. Component A comprises castor oil, a low molecular weight polyol having a molecular weight between 92 and about 200, preferably with an elastomer. Component B is

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a modified MDI, being either (i) a mix of 4,4'- and 2,4'-isomers of diphenylmethane diisocyanate or (ii) a diphenylmethane diisocyanate and its reaction product with a low molecular weight poly(oxyalkylene).

5 U.S. Patent No. 4,937,127 to Haenggi et al relates to a skid-resistant pavement marking sheet including a top surface and a plurality of skid-resistant ceramic spheroids embedded in and protruding from the surface. The ceramic spheroids are fired from a raw
10 material mixture including 10-97 weight percent mineral particulates, 3-90 weight percent alumina, and at least 1 weight percent binder, at a temperature of about 1300°C, have an outer surface rich in alumina concentration relative to the center of the spheroid, and are
15 resistant to crushing and fracturing.

SUMMARY OF THE INVENTION

It is an aspect of the present invention to
20 provide a novel epoxy composition which is generally volatile free. This composition is the reaction product of a epoxy resin, or combination of one or more resins combined with a hardener or a hardener system. The hardener can be an amine hardener such as an aliphatic
25 or aromatic amine hardener, an anhydride hardener or a mercaptan hardener, etc. It is preferable that the hardener is an amine or mercaptan. An amine hardener system comprised of more than one amine hardener is most preferred. Preferably the amine hardener system is
30 reacted with the epoxy resin at a equivalent ratio of from about 0.75 to about 1.05, and more preferably at from about 0.9 to about 1.0. The epoxy resin may include a base resin, along with an epoxy resin diluent for the reduction of the viscosity. Further, the resin
35 may contain other additives, such as pigment, thixotropic agents, defoamers, and the like.

The amine hardener system comprises one or

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more amine hardeners which are aliphatic, cycloaliphatic and/or adducts of the same. These hardeners are used at from about 15 to about 40 percent by weight of a first amine hardener (based on the total weight of the amine hardener system), which is an amino alkyl piperazine having from about 1 to about 4 carbon atoms in said alkyl group and an alkyl phenol having from about 1 to about 12 carbon atoms in said alkyl group; from about 45 to about 60 percent by weight of a second amine which is an amine derivative of ethylene, and from about 10 to about 25 percent by weight of a third amine which is an alkyl amino alkyl piperazine when all three hardeners are utilized. The hardener system further includes a catalyst which is preferably a dicarboxylic acid, and a plasticizer such as an aromatic alcohol.

The epoxy composition in accordance with this invention has a low tack-free time, appropriate color and resistance to discoloration, appropriate viscosity, adhesion to various substrates including concrete, asphalt, polyurethane and glass beads, and desirable physical properties such as good impact strength compressive and tensile strength and good abrasion resistance. Further, the epoxy provides volatile free or substantially volatile free epoxy for use in road lane markers.

The urethane composition is generally a two-part liquid system substantially free of any solvents and contains one or more polyisocyanates and one or more hydroxyl terminated intermediates. Desirably the polyisocyanate is a diisocyanate and the equivalent ratio of isocyanate groups to hydroxyl groups of the intermediate is generally from about 0.9 to about 1.5. At least some of the hydroxyl terminated intermediates have a functionality greater than two such as trifunctional compounds so that upon reaction with a diisocyanate, a cured branched or crosslinked polyurethane composition is produced. Moisture scavengers such as

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latent polyamines can also be utilized along with various catalysts and pigments. Cure generally occurs at ambient temperature. The urethane provides good weathering resistance, good abrasion resistance, good flexibility, good tensile strength and low viscosity.

5 An article is made by coating the urethane composition on the epoxy composition which generally serves as a base layer. The urethane, which is generally applied before the epoxy is fully cured and will typically bleed into, intermingle, mechanically bound, etc. with a portion of the epoxy substrate. Thus, a composite is formed from the epoxy and the urethane in which the layers are chemically fused and the layers subsequently have substantially no discrete interface but rather the composite has an intermediate section in which one or more compounds of the epoxy resin and/or hardener may join the respective polymeric units of both layers. This can generally be understood to be a form of or at least analogous to chemical bonding, to crosslinking and/or mechanically bonding between the layers. The epoxy layer generally serves as an excellent binder to the substrate as well as to optional reflective additives, i.e., glass beads, whereas the urethane layer has good abrasion resistance and good weatherability and thus can be used as a road lane marker. The combination of the epoxy and the urethane have the additional advantage that since both layers are free from volatiles, such as solvents, the final article is likewise free from volatiles. This is an advantage in the application of the laminate since it eliminates volatiles which could be hazardous to the environment or the workers who apply the laminate to the substrate surface.

30 Further, glass beads are added after application of the urethane layer in order to provide excellent nighttime and wet night reflectivity.

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DETAILED DESCRIPTION OF THE INVENTION

Articles in the form of a laminate or coated substrates are formed by generally adding a layer of the urethane composition to the epoxy composition. The epoxy composition has good bonding to surfaces such as industrial floors, garage decks, i.e. concrete and steel structures, storage tanks, roads including concrete and asphalt and the like, and hence generally serves as the substrate interface or base layer. The urethane composition has good weatherability resistance as well as generally good abrasion resistance and therefore serves as a good durable top coat.

EPOXY COMPOSITION

An epoxy composition is provided which has a unique combination of hardeners in a hardener system which are used in a specified ratio in order to achieve the properties of this composition. This epoxy composition is generally a volatile-free system. By "volatile-free system" it is meant that the composition generally contains less than 10 percent by weight of volatile, desirably less than 1 percent by weight, preferably no volatile at all, that is 0 percent, or completely free from volatile which can be released from the composition as a volatile. In the past, such volatiles have often resulted from the use of solvent. Thus, the composition is substantially, or even 100 percent non-solvent at ambient temperature and upon cure is 100 percent solids. In other words, the term "volatile-free system" can be understood to be free from organic components which have a boiling point of less than 120°F. This is also known in the art as a 100 percent solids system. This advantage results in a composition which is safer and more environmentally benign than prior art compositions. Despite this advantage, the composition has an appropriate viscosity to permit application such as by spraying.

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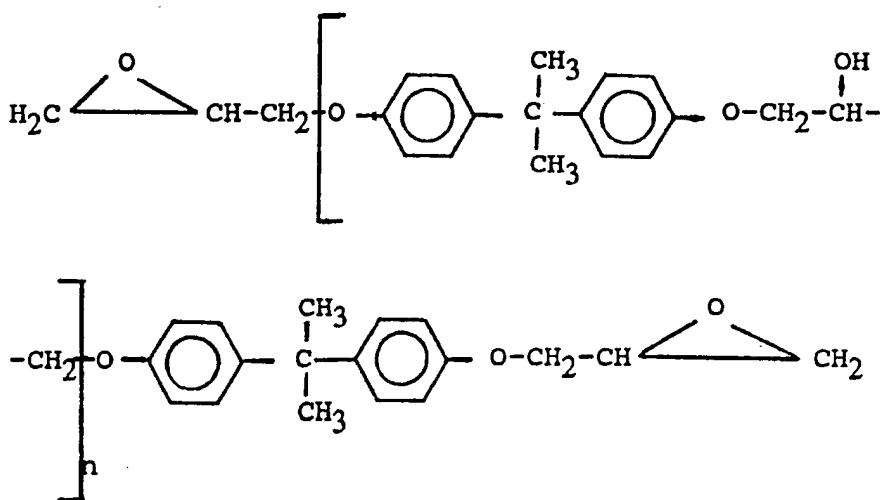
Epoxy compositions are generally formed by the mixing of two components, a part "A" comprising the epoxy resin, and a part "B" comprising the hardener system. The epoxy resin is reacted with a hardener system. In the invention, the preferred hardener is one or more amine hardeners as will be further discussed in greater detail. Such hardeners include, for example, aliphatic and aromatic amines, amine adducts, cycloaliphaticamines, mercaptans, polyamides, amidoamines, anhydrides and the like. In the present invention, one or more epoxy resin can be used as the base resin with an optional epoxy modifier and other additives.

Examples of specific epoxy resins or polymers which can be utilized include but are not limited to polyhydric phenol polyether alcohols; glycidyl ethers of novolac resins such as epoxylated phenol-formaldehyde novolac resin; glycidyl ethers of mono-, di-, and trihydric phenols; glycidyl ethers of bisphenols such as diglycidyl ether of tetrabromobisphenol A; glycidyl ethers of polynuclear phenols; epoxy resin made from diphenolic acid; glycidyl ethers of aliphatic polyols such as chlorine-containing aliphatic diepoxy and polyepichlorohydrin; glycidyl esters such as aliphatic diacid glycidyl esters and epoxidized phenolphthalein; glycidyl epoxies containing nitrogen such as glycidyl amides and amide-containing epoxies; glycidyl derivatives of cyanuric acid; glycidyl resins from melamines; glycidyl amines such as triglycidyl ether amine or p-aminophenol and bis(2,3-epoxypropyl)methylpropylammonium p-toluenesulfonate; glycidyl triazines; thioglycidyl resins such as epoxidized bisulfide; silicon-glycidyl resins such as 1,4-bis[(2,3-epoxypropoxy)dimethylsilyl]; and fluorine glycidyl resins. Other epoxy resins which can be used include those which are synthesized from mono-epoxies other than epihalohydrins including epoxy resins made from unsaturated monoepoxies such as poly-

allyl glycidyl ether and glycidyl sorbate dimer; epoxy resins from monoepoxy alcohols; epoxy resins from monoepoxies by ester interchange; epoxy resins from glycidyaldehyde; polyglycidyl compounds containing unsaturation such as allyl-substituted diglycidyl ether of bisphenol A; epoxy-resin adducts of the above; and epoxy resins which are synthesized from olefins and chloroacetyls such as butadiene dioxide, vinylcyclohexane dioxide, epoxidized polybutadiene, and bis(2,3-epoxycyclopentyl)ether. A more comprehensive list of epoxy resins can be found in Handbook of Epoxy Resins, by Henry Lee and Kris Neville, McGraw-Hill, Inc., 1967, which is hereby incorporated by reference.

The various epoxy resins or polymers which are generally applicable to the present invention as the base epoxy resin have a number average molecular weight of from about 300 to about 5,000, and preferably from about 320 to about 390. The various epoxy polymers useful for the basic epoxy resin generally are difunctional, that is, they have two epoxide groups typically at the terminal portions thereof.

A highly preferred base epoxy resin is diglycidyl ether of bisphenol A (DGEBA) which has the following formula:



wherein n is an integer from 0 to 18, desirably from

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0.05 to 3, and preferably from 0.1 to 2.

More particularly, the base epoxy resin useful for the present invention comprises a bisphenol A type resin, or a blend of bisphenol A resin and epichlorohydrin having a weight per epoxide ranging from about
5 175 to about 200, and more preferably from about 180 to about 195. The resin has a viscosity at 77°C of from about 6,000 centipoise to about 18,000 centipoises, and more preferably from about 11,000 centipoises to about
10 16,000 centipoises and most preferably from about 11,000 to about 14,000 centipoises. The resin should have a color APHA of from about 0 to about 200.

The epoxy resin can be used with a modifier such as for example a diluent. Broadly these diluents
15 should have an epoxide equivalent weight range of 120-325. In the present invention it is preferable to use an alkyl glycidyl ether as the diluent with a suitable range being from 2 to 20 carbon atoms in the alkyl portion. More preferably, the alkyl portion contains 3 to
20 10 carbon atoms, with butylglycidyl ether being most preferred. Alternatively, the diluent may be a diepoxide such as butyldiglycidyl ether. Other diluents which are applicable in the present invention include
25 cresyl diglycidyl ether having a weight equivalence of from about 160 to about 210, and more preferably from about 170 to about 195. In addition, epoxide fractions of C₂ to C₂₀ are useful with two specific fractions being in the range of C₈ to C₁₀ and in the range of C₁₂ to C₁₄ could be used. In addition, 2-ethylhexylglycidyl ether
30 could be used. When butylglycidyl ether is used, it preferably has a weight per epoxide equivalence of from about 120 to about 220, and more preferably from about 130 to about 260.

In accordance with the present invention, the
35 diluent is used in an amount sufficient to lower the viscosity of the epoxy resin to an appropriate number and will therefore of course depend upon the base resin

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used. A desired viscosity range for spray applications such as used in the present invention is from about 2,000 to about 15,000 centipoises at 77°F, and more particularly from about 3,000 to about 12,000 centipoises, and most desirably from about 4,000 to 5,000. When the base resin is bisphenol A and the diluent is butylglycidyl ether, a preferred amount of the diluent is from about 5 to about 15; preferably from about 8 to about 12; and most preferably from about 6 to about 10 parts by weight per 100 parts by weight of the epoxy base resin. The amount of the diluent added will also depend upon the amount appropriate for the addition of the pigmentation.

Other additives which can be used in the resin system include, for example, pigment. The pigment may be used, added in a desired amount, in a desired color such as for example 10 to 50; preferably 20 to 45 parts by weight per 100 parts by weight of the epoxy resins. For road marker applications in particular, a white pigment may be used which can include, for example, titanium dioxide, or a yellow pigment might be used which might include lead chromate. Of course, alternatively the epoxy can be clear, such as for a clear primer.

Other conventional additives known to the art and to the literature can be utilized such as, for example, a thixotropic agent such as amorphous fumed silica, a defoamer, heat and light stabilizers, wetting and dispersing agents, antioxidants, and the like.

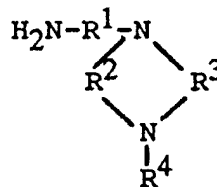
A hardener system is combined with the epoxy resin in order to produce the resultant epoxy composition. In the present invention, the hardener system utilizes one or more hardeners which could be an amine, an amidoamine, an anhydride or a mercaptan hardener. Examples of suitable mercaptans include generally mercaptan terminated polysulfides, such as LP32 and LP3 sold by Morton Thiokol, and Capcure 3800 and Capcure WR6

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5 sold by Henkel. It is preferable that the hardener is one or more amine hardeners which is either aromatic or aliphatic. Suitable aromatic hardeners include methylene dianiline, diaminodiphenylsulphone, aromatic polyamine adducts based on methylenedianiline, modified aromatic adducts based on methylenedianiline and modified methylene dianiline, and m-phenyldiamine, its adducts and derivatives and polyamines, while aliphatic hardeners include alkyl and heterocyclic amines, and their adducts and derivatives. The hardener system preferably includes more than one hardener composition in a more preferred embodiment includes at least three compositions. Thus, when the system includes a two component system, the system may be 10 to 90 percent by weight of a first hardener and 10 to 90 percent by weight of a second hardener based on the total weight of both hardeners. When the system has three or more hardeners, the system has 5 to 90 percent of a first hardener, 5 to 90 percent of a second hardener, and from 5 to 90 percent of a third hardener. In an alternative embodiment, these amine hardeners are predominately, if not exclusively, aliphatic. The amine hardeners are used in an amount so that the gram equivalent ratio of the amine functionality to the epoxide functionality of the epoxy system is from about 0.75 to about 1.05, and more preferably from about 0.9 to about 1.0. In the present application, it is preferable that three amine hardeners are used in combination in the hardener system. In particular, when the epoxy is used with a white formulation, it may be preferable that these hardeners are at least substantially aliphatic amines since aromatic amines tend to discolor.

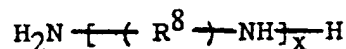
35 In a narrow embodiment, the first hardener amine (a) is a combination of an alkylphenol and a aliphatic amine which is an amino-alkyl cyclodiamine having the general formula

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5 wherein R^1 is an alkyl having 1 to 20 carbon atoms, and preferably 1 to 8 carbon atoms; and R^2 and R^3 , independently, form a heterocyclic alkyl each having 1 to 15 carbon atoms, and preferably 1 to 8 carbon atoms, and R^4 is hydrogen or R^5NH_2 or R^6NHR^7 , where R^5 is alkyl C_1 and C_{10} and preferably C_1 to C_3 , and R^6 is alkyl C_1 to C_{10} and preferably C_1 to C_3 , and R^7 is alkyl C_1 to C_{10} and preferably C_1 to C_3 . An example of a preferred cyclo-amine is amino ethyl piperazine or bis-amino propyl piperazine. A commercial example of this is Ancamine[®] 1644 sold by Pacific Anchor. Other examples would include imidazoles. This aliphatic amine is activated or modified, meaning that it is combined with an alkyl phenol having a 1 to 15 carbon alkyl, and preferably a 1 to 9 carbon alkyl, such as nonyl phenol. The combination may be an amine adduct.

15 The second amine hardener (b) is again a combination of an aliphatic amine with a phenol. The aliphatic amine could be an amine adduct. In this case the amine is a poly generic amine having the general formula

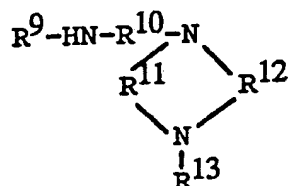


25 where R^8 is $(\text{CH}_2)_n$, where n is 1 or 2 to 30 and preferably about 2 to 12, and x is 1 to 10, preferably about 1 to 4. Preferred amines are diethylene triamine, methylenetetramine, diethylenepropylamine, tetraethylenepentaamine, and particularly preferred amines are diethylene triamine and triethylene tetramine. The phenol may include bisphenol A or bisphenol F and is preferably is bisphenol A. Again, the combination may result in an amine adduct. A commercial example of this

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is Versamine 912, sold by Henkel.

The third amine hardener (c) is preferably an alkyl amino alkyl cyclodiamine having the general formula



wherein R^9 is an alkyl having from about 1 to about 15 carbon atoms, preferably about 1 to about 10, most preferably nonyl; R^{10} is an alkyl having from about 1 to about 15; preferably from about 1 to about 8 (e.g. ethyl) and R^{11} and R^{12} together with the two amine functionalities form a heterocyclic alkyl where R^{11} and R^{12} , independently, each have from about 1 to about 15; and preferably from 1 to about 4 carbon atoms, and where R^{13} is hydrogen, or $R^{14}H_2$ or $R^{15}NHR^{16}$, where R^{14} is alkyl C_1 to C_{10} , and preferably C_1 to C_3 , and R^{15} is alkyl C_1 to C_{10} , and preferably C_1 to C_3 , and R^{16} is alkyl C_1 to C_{10} , and preferably C_1 to C_3 . Specific examples include nonylaminoethylpiperazine and bis-aminopropylpiperazine. A commercial example is Versamine 908, sold by Henkel.

The preferred amine hardeners are used in combination where, by weight, the first amine hardener (a) is from about 15 to about 40 percent; preferably from about 27 to about 37 percent; most preferably from about 29 to about 34 percent; the second amine hardener (b) is from about 45 to about 60 percent; preferably from about 46 to about 56 percent; most preferably from about 49 to about 53 percent, and the third amine hardener (c) is from about 10 to about 25 percent; preferably from about 12 to about 22 percent; most preferably from about 15 to about 20 percent, all of the foregoing percentages being by weight based on the total weight of a+b+c.

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The hardener system further includes other additives. The total hardener in the system is from about 5 to about 90 percent and more narrowly from about 10 to about 70 percent. The remainder to equal 100 percent being the other additives. One of these additives is a catalyst which is generally a dicarboxylic acid and is preferably salicylic acid. This is used in an amount of from about 2 to about 10, and preferably from about 3.5 to about 5.5 per parts by weight per 100 parts by weight of amine hardener system a+b+c.

In addition, a plasticizer may be used which is a high boiling alcohol such as the aromatic alcohols, including for example, benzyl alcohol which has a boiling point of 401°F. This is used in an amount of from about 5 to about 25; and preferably from about 10 to about 20, most preferably 15 to 20 parts by weight per 100 parts of amine hardener system (i.e. based on the total weight of a+b+c). Further, a thixotropic agent may be used in an amount to achieve the desirable viscosity which is from about 3,000 to about 8,000, centipoises. This thixotropic agent is preferably fumed silica or silicon dioxide. It is added in an amount of from about 0.5 to 5 parts; preferably from about 1 to about 4 parts by weight per 100 parts amine hardener system (a+b+c).

The hardener system achieves an appropriate color depending on the application and in particular for road markers being white and yellow, a viscosity of from about 3,000 to about 20,000 centipoises, and further desirably physical properties, such as compression set and tensile elongation. It is desirable that the compressive strength is at least 5,000, and desirably from about 12,000 psi to about 14,000 psi as compressive strength as determined by ASTM D695, and the tensile strength is at least about 5,000, and more preferably at least 6000 psi as determined by ASTM D-638.

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URETHANE COMPOSITION

The urethane composition is generally a liquid at ambient temperature, for example from about 10°C to about 40°C, and preferably from about 15°C to about 30°C. It is an important aspect of the present invention that the urethane composition be volatile-free, that is generally contains less than 10 percent by weight of volatiles therein, such as a solvent, desirably less than 1 percent by weight, and preferably no volatiles at all. Such compositions are generally described as a 100 percent solids composition. Another definition of the 100 percent volatile-free urethane system is that the system, before reaction, does not contain any components which have a boiling point of less than 120°F, even though it may be liquid. The urethane composition is the reaction of a two-part or component system, that is generally an intermediate component and a polyisocyanate component. Whenever it is desirable to prevent yellowing of the urethane composition, all components and compounds thereof are aliphatic.

Considering the intermediate component system, it can be a hydroxyl terminated lactone intermediate, and/or a hydroxyl terminated polyether, polyester, or a polyether-ester intermediate. The lactone based hydroxyl terminated compound can either be difunctional, trifunctional, tetrafunctional, or combinations thereof, for example, blends of a difunctional lactone based intermediate and a trifunctional based lactone intermediate, or the like. Hence, a lactone intermediate can have from about 2.0 to about 4.0 or preferably to about 3.0 hydroxyl groups per molecule. The hydroxyl terminated lactone intermediate is made from a lactone generally having from about 4 to about 8 carbon atoms with 6 carbons, that is caprolactone, being preferred. The lactone is typically reacted with a diol generally having from 2 to 8 carbon atoms and preferably from 2 to

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6 carbon atoms to form the hydroxyl terminated lactone intermediate. Specific examples of such diols include ethylene glycol, propylene glycol, butylene glycol such as 1,4-butane diol, hexamethylene glycol, and the like with 1,4-butanediol being preferred. When either in combination with a diol, or when used by itself, a lactone triol intermediate can be generally made from a triol having from 3 to 12 carbon atoms, desirably from 5 to 8 carbon atoms, with specific examples including glycerol, trimethylol propane, and the like. A preferred triol is 2-ethyl-2-(hydroxymethyl)1,3 propane diol, i.e., trimethylol propane. Similarly, various tetraols known to the art and to the literature can be utilized to make the lactone polyol intermediate.

Inasmuch as desirably the lactone-based diol or triol intermediate is a liquid at ambient temperature, it generally has a low molecular weight as from about 200 to about 1,000, and desirably from about 275 to about 450. Alternatively, a solid lactone intermediate may be used if it is heated above its melting point, and uniformly dispersed prior to application. However, for ease of application, the lactone is preferably a liquid at ambient temperature.

In lieu of the polylactone intermediate, or in combination therewith, a polyol intermediate can be utilized which can either be a polyester polyol, a polyether polyol, or a polyester-ether polyol intermediate. These polyol intermediates are solvent-free. The polyether intermediate is generally made from oxyalkylene compounds having from 2 to 6 carbon atoms and preferably 2 or 3 carbon atoms, i.e. specific examples include ethylene oxide, propylene oxide, butylene oxide, and the like, with ethylene oxide and propylene oxide being preferred. The ester intermediate is generally made from glycols or triols having from about 2 to about 10 and desirably from about 2 to about 6 carbon atoms, with specific examples including ethylene glycol,

propylene glycol, butylene glycol, hexamethylene glycol, trimethanol propane, and the like, with ethylene glycol and propylene glycol being preferred. The polycarboxylic acids such as a tri- or preferably dicarboxylic acids are utilized to form the ester intermediate is an aliphatic or cycloaliphatic generally containing from about 2 to about 12 carbon atoms or aromatic acids generally containing from about 8 to about 20 carbon atoms with specific examples including succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid, phthalic acid, diphenolic acid, and the like, with adipic acid and succinic acid being preferred. Although a polyether polyol or a polyester polyol can be utilized, preferably a polyester-ether intermediate is utilized made from the above ester and ether forming polyol compounds and preferably a branched polyester-ether intermediate is utilized desirably having at least two hydroxyl end groups therein. Desirably, the mixed polyester-ether is multifunctional as containing from about 2.0 to about 3.0 hydroxyl groups therein and preferably is trifunctional. An example of a highly preferred mixed polyester-ether branch polyol intermediate is Desmophen 1155 manufactured by Mobay. This intermediate has a hydroxy number of approximately 168 and an equivalent weight of 333. The equivalent weight of the polyether, the polyester, or the polyether-ester intermediate is generally from about 190 to about 500 and preferably from about 300 to about 400.

The total amount of the various one or more polyol intermediates is generally from about 30 to about 75 parts by weight, desirably from about 40 to about 60 parts, and preferably from about 45 to about 55 parts by weight for every 100 parts by weight of the entire intermediate component.

The lactone based intermediate is preferred and if another polyol intermediate is utilized in association therewith, the amount thereof is up to about

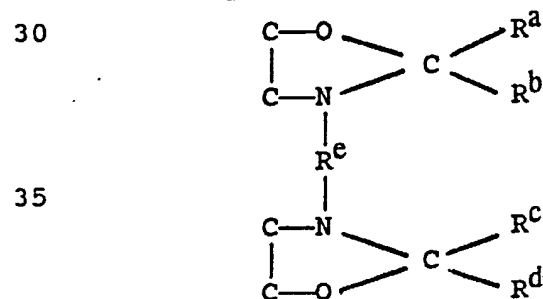
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50 percent; preferably up to about 10 percent; and most preferably up to about 6 percent by weight based upon the total weight of the lactone and the other (e.g. polyether polyol) intermediates.

5 The intermediate component also generally has a significant amount of one or more chain extenders which generally imparts stiffness to reacted urethane composition. Such chain extenders can be diols, triols, etc. having from about 2 to about 15 carbon atoms and
10 preferably from about 2 to about 6 carbon atoms with specific examples including ethylene glycol, propylene glycol, butane diol, dipropylene glycol, diethylene glycol, glycerol, trimethylol propane diol, and the like, with the diols and specifically 1,4-butane diol
15 being preferred.

The amount of the chain extender is generally from about 5 to about 25 parts, and more preferably from about 10 to about 20, and most preferably from about 14 to about 16 parts by weight for every 100 parts by
20 weight of the entire intermediate component.

In addition to the polyol intermediate and the chain extender, optionally but desirably one or more water or moisture scavengers is utilized to generally provide a moisture free composition. Such moisture
25 scavengers are generally known to the art as well as to the literature. A particular suitable moisture scavenger has been found to be a latent aliphatic polyamine which are generally the reaction of a diisocyanate with a hydroxyl terminated oxazolidine, such as



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wherein R^a , R^b , R^c , R^d , and R^e , independently, are alkyl having from 1 to 6 carbon atoms, and the diisocyanate is $R(NCO)_2$, wherein R is an aliphatic or an aromatic, or combinations thereof, generally having from about 2 to about 20 carbon atoms with specific examples including isophorone diisocyanate, hydrogenated diphenylmethane diisocyanate (HMDI), hexamethylene diisocyanate (HDI), toluene diisocyanate, and the like, but diphenylmethane diisocyanate (MDI) is generally not utilized. A desirable latent amine moisture scavenger is sold under the tradename HARDENER OZ by Mobay Chemical. Alternatively, anhydride water scavengers having a total of from 4 to 12 carbon atoms, and alkaline earth salts of such anhydrides, such as methylhexahydrophthalic anhydride sold under the tradename Luketherm-M. Other anhydrides include acetic anhydride, propionic anhydride, butyric anhydride, valeric anhydride, hexanoic anhydride, pivalic anhydride, and the like. Also molecular sieves which are generally crystalline aluminosilicates, crystalline aluminophosphates, etc. and are dispersed in a carrier oil, can be utilized. A specific example is Unisiv paste sold by UOP.

The amount of the one or more water scavengers is generally from about 1 to about 8, and preferably from about 2 to about 6 and most preferably about 3.5 to about 4.5 parts by weight for every 100 parts by weight of the entire intermediate component.

The second part of the urethane composition, that is the polyisocyanate component, i.e. $R(NCO)_n$, wherein n is from 1 to about 4 and R can be an aliphatic polyisocyanate wherein R generally contains a total of from about 2 to about 20 carbon atoms and desirably from about 4 to about 10 carbon atoms. Aromatic polyisocyanates, that is aliphatic substituted polyisocyanates such as alkyl substituted polyisocyanates, aromatic substituted aliphatic polyisocyanates, etc. can also be utilized and R generally contains a total of from 6 to

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about 20 carbon atoms. The polyisocyanate is desirably a diisocyanate, although optionally up to 10 percent by weight of a tri or tetraisocyanate can be utilized. Examples of specific aliphatic diisocyanates include the various isophorone diisocyanates (IPDI), the various hexane diisocyanates such as 1,6-hexane diisocyanate, the various mixed trimethylhexane diisocyanates, the various pentamethylene diisocyanates, and the like. Hexamethylene diisocyanate and isophorone diisocyanate are preferred. The aliphatic polyisocyanates generally have a molecular weight of from about 150 to about 600 and an equivalent weight average of from 80 to about 400. Examples of aromatic diisocyanates include para-phenylene diisocyanate, 4,4'-dibenzyl diisocyanate, dianisidene diisocyanate, meta-phenylene diisocyanate, tolylene diisocyanate, bitolylene diisocyanate, 4,4'-methylenebisphenyl isocyanate (MDI), naphthalene diisocyanate, xylene diisocyanate, and the like with MDI being preferred. The aromatic polyisocyanates generally have a molecular weight of from about 100 to about 700 and an equivalent weight average of from 80 to 300. Although aromatic type diisocyanates generally give very good properties, they tend to "yellow" the urethane composition and, hence, in various situations where color or other optical properties are important, the aliphatic polyisocyanates are preferred. The equivalent molecular ratio of NCO to OH of all of the various hydroxyl terminated intermediate compounds and chain extenders, etc., is generally a slight excess as from about 0.9 to about 1.5, desirably from about 1.02 to about 1.15, and preferably from about 1.05 to about 1.10. Ratios outside of this range generally yield a reacted product which is too flexible or too hard.

Various catalysts can be utilized such as dibutyl tin dilaurate, bismuth stearate, bismuth stannate, zinc octate, lead octate, cobalt naphthalates, and the like. The amount of such catalyst is generally

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5 small and can range from about 0 to about 2 parts by weight and preferably from about 0.1 to about 0.6 parts by weight for every 100 parts by weight of the hydroxyl containing intermediate component. In addition to promoting the reaction, the catalyst permit rapid cure at ambient temperature.

10 Various conventional additives in suitable amounts can be utilized in the intermediate component. Such additives include fillers such as clays, silicas, and the like, various antioxidants, various ultraviolet light inhibitors, air release agents, leveling agents, wetting agents, and the like, as well as pigments. With regard to road lane markers, the pigments utilized are generally titanium dioxide for white, and lead chromate and various organic pigments for yellow. Of course
15 other pigments can be utilized.

Article or Laminate

20 The epoxy composition and the urethane composition of the present invention, as noted above, are generally utilized as a laminate or layer system to form an article having good binding strength to the substrate and yet good abrasion resistance and weatherability resistance which is supplied by the urethane composition. The articles or laminates of the present invention
25 can be utilized as protective coatings for concrete floors, steel structures, storage tanks, including tanks containing corrosive material, road lane markers, and the like. These structures can be formed of various substrate materials including, for example, steel concrete and asphalt. Since the epoxy composition has
30 good bonding strength, it is generally utilized as a base or substrate interface layer.

35 The two-part epoxy system is applied by mixing both parts together in any conventional manner and applying the same to the surface to be treated or coated in any conventional manner as by brushing, spraying, and the like. The thickness of the epoxy base layer will

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vary depending upon the surface being coated and also upon the desired degree of protection sought.

5 With regard to a road lane marker, the thickness of the epoxy base layer which is applied is generally from about 5 to about 20 mils, desirably from about 8 to about 15 mils and preferably from about 10 to about 12 mils. In actual practice, the generally liquid, two-part epoxy system can be contained on a vehicle in separate tanks, subsequently mixed under high pressure and immediately thereafter applied to an appropriate position of a road to indicate a lane marker thereon. Upon a mixing of the generally liquid solvent-free two part epoxy component system, reaction immediately commences at ambient temperature. Application to the road or other substrate can be in any conventional manner as by brushing, spraying, and the like.

15 The two-part solvent free, generally liquid, urethane system which can be stored in separate containers is mixed in any convention manner, and generally applied under pressure to the top of the previously applied epoxy composition. Upon mixing, the two-part urethane system will immediately commence reaction and hence it is immediately applied to the base layer before any substantial crosslinking or curing reaction occurs. Application can be in any conventional manner as by brushing, spraying, and the like. The thickness of the urethane layer will depend upon the surface being treated and the degree of protection sought and with regard to road lane marker, the urethane is generally applied at a thickness of from about 0.5 to about 10 mils, desirably from about 0.75 to about 5 mils, and preferably 2 or 3 mils.

25 The urethane composition must be applied while the epoxy base layer is still tacky and may be cured while the epoxy system is still curing.

35 With regard to applying a lane marker to the road, the two-part urethane composition can be applied

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by a second vehicle following the first vehicle. Alternatively, the urethane composition can be contained on the same vehicle which first applies the epoxy base and shortly thereafter applies the urethane composition.

5 When the two-part urethane composition is applied to a non-fully cured epoxy coating or base layer, there might will be some bleeding or co-mingling of the urethane composition into the epoxy composition. It is desired that the epoxy base layer is not fully
10 cured when the urethane is applied so that a chemical bond will form between the layers. Because of the ingredients of both the epoxy system and the urethane system cure occurs at ambient temperatures.

 In accordance with the present invention
15 wherein the article or laminate is utilized as a road lane marker, it is highly desirable to have nighttime reflectivity. Such reflectivity is obtained by adding transparent spheres to laminate, such as ceramic spheres and preferably glass spheres. The method of application
20 generally involves simply sprinkling the spheres on the urethane layer while the same is still wet, i.e. not fully cured. Application of the spheres immediately after application of the urethane layer, e.g., from about 1 to about 10 seconds, generally results in the
25 spheres being embedded generally from about 30 to about 70 percent of the total diameter thereof, and preferably from about 40 to about 50 percent. It is desirable that the laminate is heavily embedded with the spheres. The size of the various spheres will vary according to the
30 application. Glass spheres are preferred and are readily available and generally contain a conventional sizing thereon as for example an amino silane. The present invention achieves good adhesion of the spheres as well as achieving good adhesion to the substrate.

35 The particular laminate or article of the present invention when utilized as a lane marker results in excellent adhesion to the road surface and yet offers

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excellent weatherability and abrasion resistance and is expected to yield an article having a long term life. Moreover, the glass beads have been found to have excellent adhesion to the epoxy urethane laminate.

5 The invention will be better understood by reference to the following examples but serve to illustrate, but not to limit the scope of the present invention.

Example 1

10 Preparation of the Epoxy Composition

The recipes of various components are set forth in Tables I-III and a process description for each follows:

TABLE I

Epoxy Resin Formulation, White (Part A)

15		<u>Wt. in Lbs.</u>
	Bisphenol A diglycidyl ether polymer	4114.4
	Butyl Glycidyl Ether	358.2
	Titanium-dioxide	1375.0
20	Amorphous fumed silica	82.7
	Defoamer	
		<hr/> 515.56 Ga.

25 Bisphenol A diglycidyl ether polymer (Araldite 6010), and butyl glycidyl ether (CWC-61) were mixed for eight minutes. Titanium dioxide (Ti-pure 960) and the amorphous fumed silica were added at high speed for 15-20 minutes to the above mixture. The defoamer was added and the mixture was blended at slow speed for three to

30 four minutes.

TABLE II

Epoxy Resin Formulation, Yellow (Part A)

35		<u>Wt. in Lbs.</u>
	Bisphenol A diglycidyl ether polymer	4114.4
	Butyl Glycidyl Ether	358.2
	Lead Chromate	1808.2
	Amorphous fumed silica	82.7
40	Silicon-di-oxide	
	Defoamer	
		<hr/> 515.56 Ga.

45 The process of manufacture is the same as that previously listed except that lead chromate was substituted for the titanium dioxide.

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TABLE III
Amine Hardener Formulation (Part B)

		<u>Wt. in Lbs.</u>
5	Amino-ethyl-piperazine and nonylphenol	556.27
	Diethylene Triethylene amine with bisphenol A	895.0
10	Nonyl aminoethyl piperazine	302.4
	Salicylic Acid	8.4
15	Benzyl Alcohol	291.30
	Amorphous fumed silica Silicon-di-oxide	41.0

20 The three amines (Ancamine® 1644, sold by Pacific Anchor; Versamine® 912, and Versamine® 908, respectively,) were mixed thoroughly for five to six minutes in a stainless steel tank to form Mixture 1. The benzyl alcohol and salicylic acid were mixed with

25 slow stirring and heat until the salicylic acid was dissolved to form Mixture 2. Mixture 2 was added to Mixture 1 and blended slowly for 8-10 minutes. The amorphous fumed silica was added and the mixture was blended at high speed for 15 to 20 minutes. The de-

30 foamer was added and the mixture was blended slowly for 3 to 4 minutes. The mix ratio of ether epoxy resin formulation to amine hardener formulation was 2:1 of A:B by volume. The gel time at 75°F (100 gms.) was 8-9 minutes. The tensile strength as measured by ASTM D638

35 was 6,000, the abrasion resistance as measured by ASTM C501 was about 65 mgs. The ultra violet stability as measured by ASTM-G53 was good. Shore D hardness was between about 70 and about 80 as measured by ASTM D2260 and the compressive strength as measured by ASTM D695

40 was more than 12,000 psi.

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Example 2One Component Hardener

A laboratory scale sample was made in a process similar to that set forth in Example 1, except that an epoxide fraction in the range of C₈ to C₁₀ (i.e. Heloxy 7, sold by Rhone-Poulenc) was used as a diluent rather than butyl glycidyl ether. Further, the defoamer was omitted. A one component amine hardener was used which was an aliphatic amine (i.e. Versamine 900, sold by Henkel). The specific formulation and the results are set forth in Table IV.

TABLE IV

15	<u>PART A</u>	MIX RATIO A:B::3:1 (by volume)	
	Bisphenol-A-Diglycidyl ether	282.8 gms	
	Epoxide fraction (~C ₈ -C ₁₀)	31.4 gms	
	Titanium-di-oxide	104.7 gms	
20	Amorphous fumed silica	5.9 gms	
			0.08 Gallons
	<u>PART B</u>		
25	Aliphatic Amine	108.4 gms	
			0.026 Gallons
	<u>Results</u>		
30	Gel-time at 75°F (100 gms)	30 minutes	
	Tensile strength	7000 psi	
	Abrasion resistance	154 mg	
	U.V. stability	Poor-Turns Yellow	
	Shore D hardness	70-80	

35

Example 3Two Component Hardener

A laboratory scale sample was made in a process similar to that set forth in Example 2 using a two-component hardener system, (i.e. Versamine 912, sold by Henkel and DETA-HP, sold by Pacific Anchor). The specific ratios and results are set forth in Table V.

40

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TABLE V

<u>PART A</u>		MIX RATIO A:B::2:1 (by volume)
5	Bisphenol-A-Diglycidyl ether	282.8 gms
	Epoxide fraction (~C ₈ -C ₁₀)	31.4 gms
	Titanium-di-oxide (Ti-pure 960)	104.7 gms
	Amorphous fumed silica	5.9 gms
10		<hr/> 0.08 Gallons
<u>PART B</u>		
15	Diethylenetriethyleneamine with bisphenol A	253.6 gms
	Diethylenetriamine	15.0 gms
	Salicylic acid	6.3 gms
	Benzyl alcohol	20.3 gms
	Amorphous fumed silica	5.8 gms
20		<hr/> 0.08 Gallons
<u>Results</u>		
25	Gel time at 75°F (100 gms)	8-9 minutes
	Tensile strength	5200 psi
	Compressive strength	11,000 psi
	Abrasion resistance	124 mg
	U.V. stability	acceptable
	Shore D hardness	70-80

30

Example 4Resin Modifier and Two Component Hardeners

35 A laboratory scale sample was made in a process similar to that set forth in Example 1 except that a urethane acrylate modifier was used which was Ancarez 300A, sold by Pacific Anchor. This was used with a two-component amine hardener system which was amino-ethyl-piperazine and nonylphenol and a modified cycloaliphatic (Ancamine 1895, sold by Pacific Anchor).

40 The specific formulation and results are set forth in Table VI.

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TABLE VI

<u>PART A</u>		MIX RATIO A:B::2:1 (by volume)	
5	Bisphenol-A-Diglycidyl ether	222.1 gms	
	Butyl-Glycidyl ether	14.1 gms	
	Urethane	78.7 gms	
	Titanium-di-oxide	93.6 gms	
	Amorphous fumed silica	0.2 gms	
10			0.08 Gallons
<u>PART B</u>			
15	Amino-ethyl-piperazine and nonylphenol	109.37gms	
	Modified cycloaliphatic	89.3 gms	
	Salicylic acid	7.1 gms	
	Benzyl alcohol	22.9 gms	
			0.06 Gallons
20	<u>Results</u>		
	Gel time at 75°F	8-9 minutes	
	Shore D hardness	75	
	Tensile strength	+3400 psi	
25	Compressive strength	9,000 psi	
	U.V. stability	Very poor	
		turns yellow	

Example 530 Three Component Hardeners

A laboratory scale sample was made in a process similar to that set forth in Example 2 using a three-component amine hardener system comprising diethylenetriethyleneamine with bisphenol A (Versamine 912, sold by Henkel), dimethylenetriamine (DETA-HP, sold by Pacific Anchor), and aliphatic amine (Versamine 711, sold by Henkel). The specific formulation and results are set forth in Table VII.

40

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TABLE VIIExamples of Epoxy Formulations

5	<u>PART A</u>	MIX RATIO A:B::2:1 (by volume)	
	Bisphenol-A-Diglycidyl ether	282.8 gms	
10	Epoxide fraction (C ₈ -C ₁₀)	31.4 gms	
	Titanium-di-oxide	104.7 gms	
	Amorphous fumed silica	5.9 gms	
		<hr/> 0.08 Gallons	
15	<u>PART B</u>		
	Diethylenetriethyleneamine	222.8 gms	
	Diethylenetriamine	5.1 gms	
	Aliphatic Amine	70.9 gms	
	Amorphous fumed silica	8.4 gms	
		<hr/> 0.08 Gallons	
20	<u>Results</u>		
25	Gel time at 75°F (100 gms)	8-9 minutes	
	Shore D Hardness	79	
	Tensile strength	3300 psi	
	Compressive strength	11,125 psi	
	Abrasion resistance	54 mg	
	U.V. stability	Acceptable	

Example 6Mercaptan Hardener

30 A laboratory scale sample was made as set forth generally in Example 1 using silicon dioxide and amorphous fumed silica. The formulation was combined

35 with a one-component mercaptan hardener, a mercaptan terminated polysulfide (Capcure 3-800, sold by Henke), and a trisubstituted phenol accelerator (Capcure EH-30, sold by Henkel), was also used. The specific formulation and results are set forth in Table VIII.

40

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TABLE VIII
MERCAPTAN FORMULATION

	<u>PART A</u>	MIX RATIO A:B::1:1 (by volume)	
5	Bisphenol-A-Diglycidyl ether	100 gms	
	SiO ₂ A-15)	57 gms	
	Amorphous fumed silica	8 gms	
			<hr/>
10		165 gms	
	<u>PART B</u>		
	Mercaptan terminated polysulfide	90 gms	
	Titanium-di-oxide	55 gms	
15	Amorphous fumed silica	12 gms	
	2,4,6-tri[dimethylaminomethyl]phenyl	10 gms	
			<hr/>
		168 gms	
	<u>Results</u>		
20	Gel time (100 gms)	5 minutes	
	Tensile strength	2100 psi	
	Shore D	82	
	U.V. resistance	Very poor	
25			

TABLE IX
Urethane Intermediate Formulation

		<u>Wt. in Lbs.</u>
30	2-Oxepanone, polymer with 2-ethyl-2 [hydroxy-methyl]-1,3-propane diol (polylactone intermediate) *	140.0
	Polyester-ether branch polyol intermediate **	15.6
	Hardener OZ.	10.4
35	1,4-butanediol	43.5
	Methylhexahydrophthalic anhydride	1.5
	Dibutyltindilaurate	0.88
	Titanium dioxide	69.6

Polyisocyanate Formulation

40	1,6-Hexamethylenediisocyanate based polyisocyanate ***	409.7
	* Tone 301 manufactured by Union Carbide	
	** Desmophen 1155 manufactured by Mobay (equivalent weight average 333)	
45	*** Desmodur N3200 manufactured by Mobay	

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Example 7

5 To a trimethylolpropane-caprolactone polyol [2-oxepanone, polymer with 2-ethyl-2-(hydroxymethyl)-3,3-propanediol], (Tone 301, manufactured by Union Carbide) (140.0 lbs.) was added polyesterether polyol (Desmophen 1155) (15.6 lbs.) and 1,4-butanediol (43.5 lbs.). The mixture was stirred at room temperature for 3-4 minutes. To the mixture was then added titanium dioxide (69.6 lbs.) and stirred at room temperature for 10 five minutes. To the resulting white liquid was then added a urethane bisoxazolidine (Hardener OZ., 10.4 lbs.), and methylhexahydrophthalic anhydride (Luketherm M, 1.5 lbs.) and dibutyltin dilaurate (0.88 lbs.) and the resulting mixture stirred for a further five minutes.

15 The mixture from above was reacted with one equivalent of polymeric 1,6-hexamethylenediisocyanate (Demodur N3200). The gel time for 100 gms. mixed material was 3 minutes at 25°C and the following physical properties were observed after 7 day cure: tensile 20 strength - 3,000 psi (ASTM D638), abrasion resistance <10 mg (ASTM C501) and Shore D 78 (ASTM D2260).

Example 8

25 To a trimethylolpropane-caprolactone polyol [2-oxepanone, polymer with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol] (Tone 301, 28.6 lbs.) was added 1,4-butanediol (8.0 lbs.) and the mixture stirred at room temperature for 3-4 minutes. To the mixture was then added titanium dioxide (16.6 lbs.) and the whole stirred 30 at room temperature for five minutes. To the resulting white liquid was then added a urethane bisoxazolidine (Hardener OZ, 3.0 lbs.) and methylhexahydrophthalic anhydride (Luketherm M, 0.4 lbs.) and dibutyltin dilaurate (0.2 lbs.). The resulting mixture was stirred 35 at room temperature finally for five minutes.

The mixture from above was reacted with one equivalent of polymeric 1,6-hexamethylenediisocyanate

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(Desmodur N3200). The gel time for 100 gms. mixed material was 2-1/2-3 minutes at 25°C and the following physical properties were observed after seven day cure: tensile strength 4,000 psi (ASTM D638), abrasion resistance <20 mg (ASTM C501) and Shore D 80 (ASTM D2260).

Example 9

Same as for Example 7, but 1.1 lbs. of dibutyltindilaurate was used. The resulting mixture was reacted with one equivalent of polymeric, 1,6-hexamethylenediisocyanate (Desmodur N3200). The gel time for 100 gms. mixed material was 2-2.25 mins. at 25°C and the following physical properties were observed after seven day cure: tensile strength 2,600 psi (ASTM D638), abrasion resistance <20 mg. (ASTM C501) and Shore D 79 (ASTM D2260).

Example 10

Same as for Example 8, but 0.54 lbs. of dibutyltditindilaurate was used. The resulting mixture was reacted with one equivalent of polymeric 1,6-hexamethylenediisocyanate (Desmodur N3200). The gel time for 100 gms. mixed material was 4-1/2-5 mins. at 25°C and the following physical properties were observed after seven day cure: tensile strength 3,600 psi (ASTM D638), abrasion resistance <40 mg. (ASTM C501) and Shore D 80 (ASTM D2260).

Example 11

To a trimethylolpropane-caprolactone polyol [2-oxepanone, polymer with 2 ethyl-2-(hydroxymethyl)-1,3-propanediol] (tone 301, 174.2 lbs) was added polyesterether polyol (Desmophen 1155, 42.5 lbs) and 1,4-butanediol (61 lbs.). The mixture was stirred at room temperature for .3-4 minutes. To the resulting mixture was then added titanium dioxide (92.9 lbs.) and stirred at room temperature for five minutes. To the resulting

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white liquid was then added a urethane bisoxazolidine (Hardener OZ, 13.9 lbs.), methylhexahydrophthalic anhydride (Luketherm M, 2.1 lbs.) and dibutyltin dilaurate (0.96 lbs.) and the mixture stirred for a further five minutes.

The mixture from above was reacted with a polyisocyanate mixture made by blending Desmodur N3200 (331.0 lbs.) and Desmodur KL-5-2550 (347.8 lbs.)

The gel time for 100 gms mixed material was 4 minutes at 25°C and the following physical properties were observed after 7 day cure: tensile strength - 750 psi (ASTM D638), abrasion resistance <10 mg (ASTM C501) and shore D50 (ASTM D2260).

Example 12

To a polycaprolactone diol [2-oxepanone, polymer with 2,2-oxybisethanol] (Tone 200, 57.8 lbs) was added a polycaprolactone triol [2-oxepanone, polymer with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol] (Tone 305, 358.2 lbs) and a water scavenger (Baylith Paste, 45.6 lbs). To the stirred mixture was then added a thixotropic agent (Aerosil R202, 13.1 lbs) titanium dioxide (30.4 lbs), glass microspheres (Q-Cell-600, 11.5 lbs). To the resulting white thixotropic liquid was finally added dibutyltin dilaurate (0.12 lbs).

The mixture from above was reacted with polymeric diphenylmethane diisocyanate (Mondur MRS, 290.3 lbs). The gel time for 100 gms mixed material was 4-5 minutes at 25°C and the following physical properties were observed after seven day cure: tensile strength 2600 psi (ASTM D 638), abrasion resistance <60 mg (ASTM C501) and Shore D 80 (ASTM D2260).

Example 13

To a trimethylolpropane-caprolactone polyol [2-oxepanone, polymer with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol] (Tone 305, 199.3 lbs) was added a

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polyesterether polyol (Desmophen 1150, 40.8 lbs) and a water scavenger (Baylith Paste, 25.2 lbs). To the stirred mixture was then added a thixotropic agent (Aerosil R202, 6.7 lbs), titanium dioxide (26.2 lbs) and precipitated barium sulphate (21.0 lbs). To the resulting white liquid was finally added dibutyltindilaurate (0.1 lbs).

The mixture from above was reacted with polymeric diphenylmethane diisocyanate (Mondur MRS, 162.6 lbs). The gel time for 100 gms mixed material was 5 minutes at 25°C and the following physical properties were observed after seven day cure: tensile strength 2900 psi (ASTM D638), abrasion resistance <65 mg (ASTM C501) and Shore D 75 (ASTM D2260).

Example 14

To a trimethylolpropane-caprolactone polyol [2-oxepanone, polymer with 2-ethyl-2-hydroxymethyl--1,3-propanediol] (Tone 301, 12.6 lbs) was added a polyesterether polyol (Desmophen 1145, 23.3 lbs) and 1,4-butanediol (0.70 lbs). To the stirred mixture was then added a urethane bisoxazolidine (Hardener OZ, 1.5 lbs) and methylhexahydrophthalic anhydride (Lukethen M, 0.21 lbs). To the resulting mixture was added titanium dioxide (15.8 lbs) and stirred for five minutes. Finally dibutyltindilaurate was added (0.28 lbs), and mixed for a further five minutes.

The mixture from above was reacted with 45.9 lbs of polymeric 1,6-hexamethylene diisocyanate Desmodur N3200. The gel time for 100 gms mixed material was 5 minutes at 25°C and the following physical properties were observed after seven day cure: tensile strength 2600 psi (ASTM D 638), abrasion resistance <20 mg (ASTM C501) and Shore D 70.

(Composite) Example 15

An epoxy coating as described in Example 1 was

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5 cured with hardener described in Example 1 and applied
at thickness of 12 mils. Immediately on top was placed
a polyurethane coating prepared as described in Example
7. The polyurethane coating was applied at a thickness
of 3-4 mils. The composite coating was cured for 3 days
at room temperature and then found to give the following
properties: Abrasion resistance <10 mg (ASTM C501);
adhesion to concrete: failure in concrete (ACI 503);
weathering resistance: no change in color after 750
10 hours, 4 hours humidity, 50°C, 4 hours UV (ASTM-G53).
The test was stopped prior to discoloration.

(Composite) Example 16

15 Essentially prepared as Example 15, but after
the polyurethane coating had been applied glass beads
were also applied. After 3-day cure at room tempera-
ture, the composite was found to show no change in color
when subjected to accelerated weathering as described in
Example 15.

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Comparative Example 17

For the purpose of comparison, a commercially
available long-lived prior art sample based on an epoxy
system made by Poly-Carb was tested and found to discol-
25 or under acceleration within 72 hours! In contrast, the
invention demonstrates an improvement of well more than
10 times in the resistance to discoloration. This
results in increased maintenance of optical properties.

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Example 18

To an industrial concrete floor was applied an
epoxy coating prepared as described in Example 5 at a
thickness of 5 mils. Just prior to the epoxy coating
becoming tack free, a polyurethane coating prepared as
described in Example 13 was applied on it at a thickness
35 of approximately 10 mils.

The flooring system was allowed to cure at

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25°C for 12 hours and the floor returned to its normal use. The floor system was found to be aesthetically pleasing, self-leveled, easy to maintain with excellent abrasion, and impact properties as well as good chemical resistance.

DISCUSSION OF THE RESULTS

The foregoing examples illustrate the advantages of the present invention. Specifically, the present invention has no volatile organic components. The organic structure when based on aliphatic compositions rather than aromatic compositions has superior weatherability and resistance to discoloration. The intermediate isocyanate chemistry results in a urethane which is flexible and yet tough to very rigid by varying the chain length of either the intermediate or the isocyanate prepolymers or monomers. The resulting composition has excellent physical properties for the intended use as well good chemical properties. The method of application results in a permanent chemical fusion between the layers. The epoxy layer has good wetability, while the urethane layer allows for a short tack free time. The short tack free time limits the amount of time that dirt can make it onto the surface, and shortens the time before cars can drive on the surface. The chemical fusion between the layers can be understood as the chemical reaction between the two layers which becomes a part of the polymeric structure having no discrete interface, but a form of crosslinking between the layers. It is possible to drive over the present composition within 5 to 10 minutes without harming the composition, whereas in contrast, in the past it has been necessary to wait a cure time of 60 to 75 minutes.

While in accordance with the Patent Statutes, the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

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WHAT IS CLAIMED IS:

URETHANE CLAIMS:

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1. A two-part urethane composition, comprising;

an intermediate component and a polyisocyanate component;

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said intermediate component comprising a lactone polyol, a polyether polyol, a polyester polyol, or a polyether-ester polyol, or combinations thereof, and a chain extender,

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said polyisocyanate component being an aromatic, an aliphatic polyisocyanate, or combinations thereof, and wherein the two-part urethane composition contains less than 10 percent by weight of volatiles therein.

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2. A two-part urethane composition according to Claim 1, wherein said lactone intermediate is made from a lactone having from 4 to 8 carbon atoms which is reacted with a polyol having from 2 to 4 hydroxyl groups and from 2 to 12 carbon atoms, wherein said polyether polyol is made from an oxyalkylene having from 2 to 6 carbon atoms, and wherein said polyester polyol is made from a diol or triol, or combinations thereof, having a total of from 2 to 12 carbon atoms and a dicarboxylic acid having a total of from about 2 to about 12 carbon atoms, and wherein said polyether-ester polyol is made from said ether and ester polyol forming compounds, and wherein the equivalent molecular ratio of said isocyanate to said hydroxyl of all said hydroxyl terminated compounds is from about 0.9 to about 1.5, and wherein said volatile has a boiling point of less than 120°F.

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3. A two-part urethane composition according

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to Claim 2, wherein the amount of said polyol intermediate is from about 30 parts to about 75 parts by weight for every 100 parts by weight of said intermediate component, wherein the molecular weight of said lactone intermediate is from about 200 to about 1,000, wherein the equivalent weight of said polyether polyol, said polyester polyol, or said polyether-ester polyol is from about 190 to about 500, wherein said chain extender is a diol or a triol having from 2 to 15 carbon atoms, wherein the amount of said chain extender is from about 5 to about 25 parts by weight for every 100 parts by weight of said intermediate component; and from about 1.0 to about 8.0 parts by weight for every 100 parts by weight of the intermediate component of one or more moisture scavengers.

4. A two-part urethane composition according to Claim 3, wherein said polyol intermediate is said lactone polyol containing up to about 10 percent by weight of said polyether polyol, said polyester polyol, or said polyester-ether polyol intermediate, wherein said moisture scavenger is an aliphatic polyamine, an anhydride, or a molecular sieve, and wherein the ratio of said isocyanate to said hydroxyl is from about 1.02 to about 1.15.

5. A two-part urethane composition according to Claim 4, wherein the amount of said volatile component is less than 1 percent by weight, wherein said lactone has from about 2.0 to about 3.0 hydroxyl groups per molecule, wherein the amount of said lactone intermediate is from about 40 to about 60 parts by weight; wherein said polyisocyanate is a diisocyanate containing less than 10 percent by weight of a triisocyanate or a tetraisocyanate, wherein said chain extender is a diol having from 2 to 6 carbon atoms, and wherein said moisture scavenger is said aliphatic polyamine which is

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the reaction product of an oxazolidine and a diisocyanate, wherein said anhydride moisture scavenger is an anhydride or an alkaline earth salt thereof having a total of from 2 to 12 carbon atoms, or said molecular sieve.

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6. A two-part urethane composition according to Claim 5, wherein said moisture scavenger is methylhexahydrophthalic anhydride or said aliphatic polyamine, wherein the molecular weight of said lactone intermediate is from about 275 to about 450, wherein the amount of said lactone intermediate is from about 45 to about 55 parts by weight, wherein said lactone is a) 2-oxepanone polymer with 2-ethyl-2(hydroxy-methyl)-1,3-propane diol, and wherein said isocyanate/hydroxyl ratio is from about 1.05 to about 1.10, and wherein said urethane composition is free of volatiles having a boiling point of less than 120°F.

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7. A two-part urethane composition according to Claim 1, wherein said polyisocyanate is an aliphatic isocyanate.

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8. A two-part urethane composition according to Claim 3, wherein said polyisocyanate is an aliphatic isocyanate.

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9. A two-part urethane composition according to Claim 5, wherein said polyisocyanate is an aliphatic diisocyanate having from 4 to 10 carbon atoms.

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10. A two-part urethane composition according to Claim 7, wherein said polyisocyanate is 1,6-hexamethylene-diisocyanate based polyisocyanate, isophorone diisocyanate, or combinations thereof.

11. A urethane composition, comprising the

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cured urethane composition of Claim 1.

12. A urethane composition, comprising the cured urethane composition of Claim 3.

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13. A urethane composition, comprising the cured urethane composition of Claim 6.

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14. A urethane composition, comprising the cured urethane composition of Claim 7.

15. A urethane composition, comprising the cured urethane composition of Claim 9.

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16. A urethane composition, comprising the cured urethane composition of Claim 10.

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17. A cured urethane composition, comprising the reaction product of;

an intermediate component and a polyisocyanate component; said intermediate component comprising a lactone polyol, a polyether polyol, a polyester polyol, or a polyether-ester polyol, or combinations thereof, and a chain extender,

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said polyisocyanate component being an aromatic, an aliphatic polyisocyanate, or combinations thereof, and wherein the cured urethane composition is substantially volatile free.

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18. A cured urethane composition according to Claim 17, wherein said lactone intermediate is made from a lactone having from 4 to 8 carbon atoms which is reacted with a polyol having from 2 to 4 hydroxyl groups and from 2 to 12 carbon atoms, wherein said polyether polyol is made from an oxyalkylene having from 2 to 6 carbon atoms, and wherein said polyester polyol is made from a diol or triol, or combinations thereof, having a

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total of from 2 to 12 carbon atoms and a dicarboxylic acid having a total of from about 2 to about 12 carbon atoms, and wherein said polyether-ester polyol is made from said ether and ester polyol forming compounds, and wherein the equivalent molecular ratio of said isocyanate to said hydroxyl of all said hydroxyl terminated compounds is from about 0.9 to about 1.5.

19. A cured urethane composition according to Claim 18, wherein the amount of said lactone intermediate is from about 30 parts to about 75 parts by weight for every 100 parts by weight of said intermediate component, wherein the molecular weight of said lactone intermediate is from about 200 to about 1,000, wherein the equivalent weight of said polyether polyol, said polyester polyol, or said polyether-ester polyol, is from about 190 to about 500, wherein said chain extender is a diol or a triol having from 2 to 15 carbon atoms, wherein the amount of said chain extender is from about 5 to about 25 parts by weight for every 100 parts by weight of said intermediate component; and from about 1.0 to about 8.0 parts by weight for every 100 parts by weight of the intermediate component of one or more moisture scavengers.

20. A cured urethane composition according to Claim 19, wherein said polyisocyanate is an aliphatic isocyanate, and wherein said polyol intermediate is said lactone polyol.

21. An article comprising, an epoxy coat and a urethane coat thereon, said epoxy coat being a substantially volatile free system, and said urethane being the reaction product of a two part, substantially volatile free system.

22. An article as set forth in Claim 21,

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wherein said epoxy coat is in immediate contact with said urethane coat.

5 23. An article as set forth in Claim 22, wherein upon curing said epoxy coat is chemically fused with said urethane coat.

10 24. An article as set forth in Claim 23, further including one or more reflective agents.

 25. An article as set forth in Claim 24, wherein said one or more reflective agents comprises glass spheres.

15 26. An article as set forth in Claim 23, wherein said epoxy system is applied at a thickness of from about 5 to about 20 mils and said urethane system is applied at a thickness of from about 0.5 to about 10 mils.

20 27. An article as set forth in Claim 26, wherein said epoxy system is applied at a thickness of from about 8 to about 15 mils and said urethane system is applied at a thickness of from about 0.75 to about 5 mils.

25 28. An article as set forth in Claim 27, wherein said epoxy system is applied at a thickness of from about 10 to about 12 mils and said urethane system is applied at a thickness of from about 2 to about 3 mils.

30 29. An article as set forth in Claim 23, wherein said two part epoxy system comprises an epoxy resin and an epoxy hardener system, said hardener system comprising at least one amine or mercaptan hardener.

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30. An article as set forth in Claim 29, wherein said epoxy hardener system comprises at least an amine hardener (a) and an amine hardener (b), and said amine hardener (a) is from about 10 to about 90 percent by weight of a+b and said amine hardener (b) is from about 10 to about 90 percent by weight of a+b.

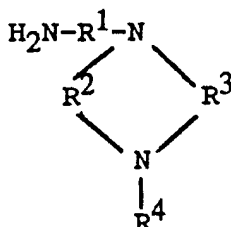
31. An article as set forth in Claim 30, wherein said urethane is the reaction product of polyisocyanate component and an intermediate component comprising a lactone polyol, a polyether polyol, a polyester polyol, a polyether-ester polyol, or combinations thereof.

32. An article as set forth in Claim 31, wherein said intermediate component further comprises a chain extender and a latent aliphatic polyamine.

33. An article as set forth in Claim 23, wherein said hardener system comprises at least three amine hardeners, wherein the first amine hardener (a) is from about 5 to about 90 percent by weight, the second amine hardener (b) is from about 5 to about 90 percent by weight, and the third amine hardener (c) is from about 5 to about 90 percent by weight; all percentages being based upon the weight of a+b+c.

34. An article as set forth in Claim 33, wherein the hardener system comprises:
said first hardener amine which comprises a combination of an alkylphenol and an aliphatic amine which is an aminoalkyl cyclodiamine having the general formula

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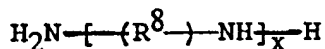
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wherein R^1 is an alkyl having 1 to 20 carbon atoms, and
 R^2 and R^3 , independently, form a heterocyclic alkyl
 having 1 to 15 carbon atoms, and R^4 , where R^4 is hydrogen
 or R^5NH_2 or R^6NHR^7 , where R^5 is alkyl having 1 to 10
 carbon atoms, where R^6 and R^7 , independently, are alkyl
 having 1 to 10 carbon atoms, said alkyl group of said
 alkyl phenol having from 1 to 15 carbon atoms, and

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said second amine hardener which comprises a
 combination of an aliphatic amine with a phenol, the
 aliphatic amine comprising a polygeneric amine having
 the general formula

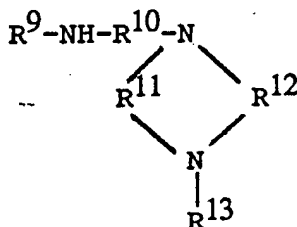
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where R^8 is $(\text{CH}_2)_n$, where n is 1 to 30, x is 1 to 10, and

said three amine hardener has the general
 formula

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where R^9 is alkyl having 1 to 10 carbon atoms and
 wherein R^{10} is alkyl having 1 to 10 carbon atoms, R^{11} and
 R^{12} together with the two amine functionalities form a
 heterocyclic alkyl where R^{11} and R^{12} are each aliphatic,
 and R^{13} is hydrogen or R^{14}NH_2 or $\text{R}^{15}\text{NHR}^{16}$, where R^{14} is an
 alkyl having 1 to 10 carbon atoms, and R^{15} is an alkyl
 having 1 to 10 carbon atoms, and R^{16} is alkyl having 1 to
 10 carbon atoms.

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35. The article as set forth in Claim 34, wherein:

the first amine hardener (a) is from about 15 to about 40 percent, the second amine hardener (b) is from about 45 to about 60 percent, and the third amine hardener (c) is from about 10 to about 25 percent, all of the foregoing percentages being by weight based on the total weight of a+b+c.

36. An article as set forth in Claim 35, wherein said epoxy resin comprises from about 85 to about 95 percent of a base resin (A) and from about 5 to about 15 percent of a diluent (B), said percent being a weight percent based on the total of A and B, and said epoxy resin having a viscosity of from about 500 to about 25,000 centipoises.

37. An article as set forth in Claim 36, wherein said base resin comprises the glycidyl ether of bisphenol A and said diluent comprises dibutylglycidyl ether.

38. An article as set forth in Claim 37, wherein said first amine hardener comprises a combination of amino ethyl piperazine and nonyl phenol; said second amine hardener comprises a combination of bisphenol A and diethylenetriamine, and said third amine hardener comprises nonylaminoethylpiperazine.

39. An article as set forth in Claim 31, wherein said lactone polyol is made from a lactone having from 4 to 8 carbon atoms which is reacted with a polyol having from 2 to 4 hydroxyl groups and from 2 to 12 carbon atoms, wherein said polyether polyol is made from an oxyalkylene having from 2 to 6 carbon atoms, and wherein said polyester polyol is made from a diol or triol, or combinations thereof, having a total of from

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2 to 12 carbon atoms and a dicarboxylic acid having a total of from about 2 to about 12 carbon atoms, and wherein said polyether-ester polyol is made from said ether and ester polyol forming compounds, and wherein
5 the equivalent molecular ratio of said isocyanate to said hydroxyl of all said hydroxyl terminated compounds is from about 0.9 to about 1.5, and wherein said volatile has a boiling point of less than 120°F.

10 40. An article as set forth in Claim 33, wherein said intermediate component further comprises a chain extender and wherein the amount of said lactone intermediate is from about 30 parts to about 75 parts by weight for every 100 parts by weight of said intermediate component, wherein the molecular weight of said
15 lactone intermediate is from about 200 to about 1,000, wherein the equivalent weight of said polyether polyol, said polyester polyol, or said polyether-ester polyol is from about 190 to about 500, wherein said chain extender
20 is a diol or a triol having from 2 to 15 carbon atoms, wherein the amount of said chain extender is from about 5 to about 25 parts by weight for every 100 parts by weight of said intermediate component; and from about 1.0 to about 8.0 parts by weight for every 100 parts by
25 weight of the intermediate component of one or more moisture scavengers.

41. An article as set forth in Claim 35, wherein said polyol intermediate is said lactone polyol
30 containing up to about 10 percent by weight of said polyether polyol, said polyester polyol, or said polyester-ether polyol, wherein said moisture scavenger is an aliphatic polyamine, an anhydride, or a molecular sieve, and wherein the ratio of said isocyanate to said hydroxyl
35 is from about 1.02 to about 1.15.

42. An article as set forth in Claim 37,

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wherein the amount of said volatile component is less than 1 percent by weight, wherein said lactone has from about 2.0 to about 3.0 hydroxyl groups per molecule, wherein the amount of said lactone intermediate is from about 40 to about 60 parts by weight; wherein said polyisocyanate is a diisocyanate containing less than 10 percent by weight of a triisocyanate or a tetra-isocyanate, wherein said chain extender is a diol having from 2 to 6 carbon atoms, and wherein said moisture scavenger is said aliphatic polyamine which is the reaction product of an oxazolidine and a diisocyanate, wherein said anhydride moisture scavenger is an anhydride or an alkaline earth salt thereof having a total of from 2 to 12 carbon atoms, or said molecular sieve.

43. An article as set forth in Claim 39, wherein said moisture scavenger is methylhexahydrophthalic anhydride or said aliphatic polyamine, wherein the molecular weight of said lactone intermediate is from about 275 to about 450, wherein the amount of said lactone intermediate is from about 45 to about 55 parts by weight, wherein said lactone is a) 2-oxepanone polymer with 2-ethyl-2 (hydroxy-methyl)-1,3-propane diol, and wherein said isocyanate/hydroxyl ratio is from about 1.05 to about 1.10, and wherein said urethane composition is free of volatiles having a boiling point of less than 120°F.

44. An article comprising an epoxy coat and a urethane coat, said epoxy coat comprising:
the reaction product of an epoxy resin and a hardener system, said resin having an epoxide equivalent of from about 0.2 to about 0.8, and said hardener having a free hydrogen equivalent of from about 65 to about 125, said hardener system being present in an amount of from about 0.3 to about 0.5 parts per part epoxide resin wherein said epoxide resin comprises one or more base

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resins of the glycidyl ether of bisphenol A, or butyl glycidyl ether, and a diluent comprising one or more epoxy resins of butyl glycidyl ether or butyl diglycidyl ether, and cresyl diglycidyl ether, said epoxy resin having a viscosity of from about 1 cps to about 30 cps and said hardener system comprising the combination of at least a first, a second, and a third amine hardener, said first amine hardener comprising the combination of an alkyl phenol and an aliphatic amine, said second amine hardener comprising the combination of a polygeneric amine and a phenol, and said third amine hardener comprising an alkyl amino alkyl cyclodiamine; and

said urethane coat comprising the reaction product of an aliphatic polyisocyanate component and an intermediate component, said intermediate component comprising a hydroxyl terminated aliphatic polylactone, an aliphatic polyol chain extender, and a moisture scavenger.

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45. An article as set forth in Claim 44, wherein said epoxy coat is adhered to a substrate comprising concrete or asphalt.

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46. An article as set forth in Claim 21, wherein said article is a roadlane marker.

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47. An article as set forth in Claim 24, wherein said article is a roadlane marker.

48. An article as set forth in Claim 26, wherein said article is a roadlane marker.

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49. An article as set forth in Claim 32, wherein said article is a roadlane marker.

50. An article as set forth in Claim 34,

- 50 -

wherein said article is a roadlane marker.

51. An article as set forth in Claim 44, wherein said article is a roadlane marker.

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52. A volatile-free composition comprising an epoxy resin and an epoxy hardener system, said hardener system comprising at least one hardener which is an amine hardener or a mercaptan hardener.

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53. A volatile-free epoxy composition as set forth in Claim 52, wherein said hardener system comprises at least a first amine hardener (a) at from about 10 to about 90 percent and at least a second amine hardener (b) at from about 10 to about 90 percent, said percentages being by weight based on the total amount of a+b.

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54. A volatile-free epoxy composition as set forth in Claim 53, wherein said hardener system comprises at least a first amine hardener (a) at from about 5 to about 90 percent, at least a second amine hardener (b) at from about 5 to about 90 percent, and at least a third amine hardener (c) at from about 5 to about 90 percent, said percentages being by weight based on the total amount of a+b+c.

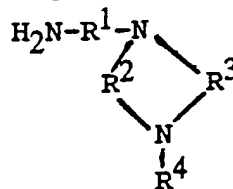
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55. An epoxy composition as set forth in Claim 54, wherein said hardener system comprises:

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(a) from about 15 to about 40 percent of said first amine hardener comprising a combination of an alkylphenol and a aliphatic amine which is an amino-alkyl cyclodiamine having the general formula



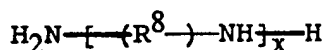
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wherein R^1 is an alkyl having 1 to 20 carbon atoms, and

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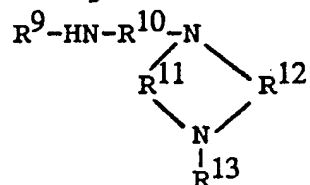
R^2 and R^3 , independently, form a heterocyclic alkyl having 1 to 15 carbon atoms, and R^4 is hydrogen or R^5NH_2 or R^6NHR^7 , where R^5 is alkyl having 1 to 10 carbon atoms, and R^6 is alkyl having 1 to 10 carbon atoms, and R^7 is alkyl having 1 to 10 carbon atoms, said alkyl group of said alkyl phenol has from 1 to 15 carbon atoms, and

from about 45 to about 60 percent of said second amine hardener which comprises a combination of an aliphatic amine with a phenol, the aliphatic amine comprising a poly generic amine having the general formula



where R^8 is $(CH_2)_n$, where n is 1 to 30, x is 1 to 10, and

from about 10 to about 25 percent of said third amine hardener which comprises an alkyl amino alkyl cyclodiamine having the general formula



wherein R^9 is an alkyl having about 1 to about 10 carbon atoms, R^{10} is an alkyl having from about 1 to about 15 carbon atoms; and R^{11} and R^{12} together with the two amine functionalities form a heterocyclic alkyl where R^{11} and R^{12} are each aliphatic having from about 1 to about 15, and R^{13} is hydrogen or $R^{14}NH_2$ or $R^{15}NHR^{16}$, where R^{14} is alkyl having 1 to 10 carbon atoms, R^{15} is alkyl having 1 to 10 carbon atoms, and R^{16} is alkyl having 1 to 10 carbon atoms, said percentages being by weight based upon the total of $a+b+c$.

56. The epoxy composition as set forth in Claim 55, wherein:

the first amine hardener (a) is from about 27 to about 30 percent, the second amine hardener (b) is

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from about 66 to about 56 percent, and the third amine hardener (c) is from about 12 to about 22 percent, all of the foregoing percentages being by weight based on the total weight of a+b+c.

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57. An epoxy composition as set forth in Claim 52, wherein said epoxy resin further includes a pigment, and said composition achieves good adhesion to a concrete or asphalt surface.

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58. An epoxy composition as set forth in Claim 56, wherein said epoxy resin is one or more resins of bisphenol A, bisphenol F resin based on novolac, and diglycidyl ether, and wherein said hardener system is present at an available hydrogen per epoxide equivalent of from about 0.9 to about 1.1.

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59. An epoxy composition as set forth in Claim 58, wherein said first amine hardener comprises one or more modified aliphatic amine and is reacted in an amount consisting of from about 29 to about 34 percent, said second amine hardener comprises one or more modified amine and is reacted in an amount consisting of from about 49 to about 53 percent; and said third amine hardener is reacted in an amount consisting of from about 15 to about 20 percent, said percentage being by weight based on the total weight of a+b+c.

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60. An epoxy composition as set forth in Claim 59, wherein said epoxy resin comprises from about 85 to about 95 percent of a base resin (A) and from about 5 to about 15 percent of a diluent (B), said percent being a weight percent based on the total of A and B, and said epoxy resin having a viscosity of from about 500 to about 25,000 centipoises.

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61. An epoxy composition as set forth in

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Claim 55, wherein said first amine hardener comprises one or more modified aliphatic amine; said second amine hardener comprises one or more modified amine; and said third amine hardener comprises one or more modified amine.

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62. An epoxy composition as set forth in Claim 61, wherein said hardener further includes catalyst comprising a dicarboxylic acid, and a thixotropic agent.

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63. An epoxy composition as set forth in Claim 62, wherein said base resin comprises bisphenol A and said diluent comprises dibutylglycidyl ether.

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64. An epoxy composition as set forth in Claim 63, wherein said first amine hardener comprises a combination of amino ethyl piperazine and nonyl phenol; said second amine hardener comprises a combination of bisphenol A and diethylene triethylene amine, and said third amine hardener comprises nonylaminoethyl piperazine.

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65. An epoxy composition as set forth in Claim 64, wherein said epoxy resin further comprises a pigment comprising one or more of lead chromate and titanium dioxide.

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66. An epoxy composition as set forth in Claim 65, wherein said composition achieves an adhesion to glass beads and an adhesion to concrete, of from about 300 psi to about 100 percent failure in concrete or asphalt.

30

67. An epoxy composition which is the reaction product of an epoxy resin, and a hardener system, said resin having an epoxide equivalent of from about

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0.2 to about 0.8, and said hardener having a free hydrogen equivalent of from about 20 to about 200, said hardener system being present in an amount of from about 0.3 to about 0.5 parts per part epoxide resin wherein said epoxide resin comprises one or more base resins of the glycidyl ether of bisphenol A or butyl glycidyl ether, and a diluent comprising butyl glycidyl ether, butyl diglycidyl ether, or cresyl diglycidyl ether, 2-ethylhexylglycidyl ether, cresyl diglycidyl ether, or epoxide fractions in the range of about C₈ to C₂₀, said epoxy resin having a viscosity of from about 1 cps to about 300 cps;

said hardener system comprising the combination of at least a first, a second, and a third amine hardener, said first amine hardener comprising the combination of an alkyl phenol and aliphatic amines, said second amine hardener comprising the combination of a polygeneric amine and a phenol, and said third amine hardener comprising an alkyl amino alkyl cyclodiamine.

68. An epoxy composition as set forth in Claim 67, wherein said first amine hardener (a) is present at from about 29 to about 34 percent, said second amine hardener (b) is present at from about 49 to about 53 percent, and said third amine hardener (c) is present at from about 15 to about 20 percent, said percentages being based on the total weight of (a), (b) and (c).

69. An epoxy composition as set forth in Claim 68, wherein said hardener system further comprises a catalyst which is a dicarboxylic acid.

70. An epoxy composition as set forth in Claim 69, wherein said base resin has a molecular weight of from about 320 to about 390, said diluent has a molecular weight of from about 300 to about 800.

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71. An epoxy composition as set forth in Claim 70, wherein said epoxy resin further includes a pigment.

5 72. An epoxy composition as set forth in Claim 71, wherein said composition further includes reflective agents.

10 73. A method of forming a coating composition comprising the steps of applying a first layer to a substrate, the first layer comprising an epoxy composition which is the reaction product of an epoxy resin and an epoxy hardener system, said hardener system comprising at least a first amine or mercaptan hardener and
15 applying a urethane composition comprising the reaction product of an an aliphatic polylactone polyol, an aliphatic polyol chain extender, and a moisture scavenger, said urethane being applied to said epoxy composition prior to the cure of said epoxy composition.

20 74. A method as set forth in Claim 73, wherein said process further includes the step of applying a reflective agent to said urethane coat prior to said urethane coat curing.

25 75. A method as set forth in Claim 74, wherein said urethane coat is saturated with said reflective agent.

30 76. A method as set forth in Claim 75, wherein said reflective agent is glass beads.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/09941

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08G 59/00, 18/10; B05D 1/36, 5/10; B32B 27/38, 27/40, 17/10

US CL :528/87, 60; 427/407.1, 136, 138; 428/413, 423.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/87, 60; 427/407.1, 136, 138; 428/413, 423.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	"Concrete Coating Combine Compliance and Performance in Modern Paint Coatings" 1991 (FERRELL) see Abstract and pages 48-50.	21-51
Y	US,A, 4,689,268 (MEADER, JR.) 25 August 1987 see entire document.	21-51
Y	US,A, 4,699,814 (AMBROSE et al.) 13 October 1987 see entire document.	21-51
Y	US,A, 4,877,829 (VU et al.) 31 October 1989 see entire document.	21-51
A	US,A, 3,136,733 (ROSS et al.) 09 June 1964 see entire document.	1-76

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

01 JANUARY 1993

Date of mailing of the international search report

01 APR 1993

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/09941

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,554,214 (ICHINOMIYA et al.) 19 November 1985 see entire document.	1-76
A	US,A, 4,732,790 (BLACKBURN et al.) 22 March 1988 see entire document.	1-76
A	US,A, 4,758,469 (LANGE) 19 July 1988 see entire document.	1-76
A	US,A, 4,837,069 (BESCUP et al.) 06 June 1989 see entire document.	1-76
A	US,A, 4,859,735 (VU) 22 August 1989 see entire document.	1-76
A	US,A, 4,937,127 (HAENGGI et al.) 26 June 1990 see entire document.	1-76

INTERNATIONAL SEARCH REPORT

Int. national application No.
PCT/US92/09941**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
(Telephone Practice)
Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/09941

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- I. Claims 1-20, drawn to a two-part urethane composition and the cured product thereof classified in Class 528, subclass 60.
- II. Claims 21-51, drawn to an article of manufacture containing an epoxy coat and a urethane coat classified in Class 428, subclass 423.1.
- III. Claims 52-72 drawn to an epoxy composition classified in Class 528, subclass 87.
- IV. Claims 73-76 drawn to a method of coating classified in Class 427, subclass 407.1.

Groups I and II are related as combination subcombination but the combination does not require the particulars of the subcombination as claimed for patentability as evidenced by claim 21 which recites the urethane composition broadly. The subcombination has utility by itself or in other different combinations and is well known in the art.

Groups II and III are related as combination subcombination but lack unity for the same reasons stated above.

Groups I, II, III and IV are related as product and process of using. The three products are patentably distinct from each other and each may be used in a materially different process of using than that claimed.

The inventions as above grouped are not so linked as to form a single inventive concept as required by PCT Rule 13.2. There is no evidence of a special technical feature common to the inventions as above grouped.